Electric Field Gradients at ^{57}Fe in ZnFe$_2$O$_4$ and CdFe$_2$O$_4$

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The nuclear quadrupole coupling constants and isomer shifts of ^{57}Fe in the spinels ZnFe$_2$O$_4$ and CdFe$_2$O$_4$ were measured using the Mössbauer effect. The signs of the quadrupole coupling constants were determined from spectra which were taken in an applied magnetic field. The sign is negative in both spinels. The isomer shifts and Fe–O distances indicate that Fe^{3+} in ZnFe$_2$O$_4$ is somewhat more covalently bonded than in CdFe$_2$O$_4$. The external field gradients at the Fe^{3+} positions can be interpreted in terms of the ionic point-multipole model modified by some charge transfer between oxygen and the cations. The point charge contribution to the field gradient is positive in case of ZnFe$_2$O$_4$ and nearly zero in case of CdFe$_2$O$_4$; the predominant contribution is due to the electric dipole moments of the oxygen ions and is negative. The dipole polarizability of the oxygen ion which gave the best fit is $\alpha_D = 0.8$ Å^3. The effect of charge transfer on the ionic field gradient is small.

INTRODUCTION

Recently the nuclear quadrupole interaction of ^{57}Fe in the spinel ferrites ZnFe$_2$O$_4$ and CdFe$_2$O$_4$ has been studied using Mössbauer spectroscopy.[1–4] Hudson and Whitfield[1] determined the quadrupole coupling constant and isomer shift of ^{57}Fe in ZnFe$_2$O$_4$ and CdFe$_2$O$_4$ at 22°C. Yagnik and Mathur[2] measured these parameters in solid solutions (Zn, Cd)Fe$_2$O$_4$ at 22°C. Earlier, Mizoguchi and Tanaka[3] had investigated the quadrupole coupling constant and isomer shift in ZnFe$_2$O$_4$ at temperatures between 26 and 510°C. Since the spectra in these studies were taken at temperatures above the Néel point, which is lower than 20°K in both spinels, the sign of the quadrupole coupling constant could not be determined.

ZnFe$_2$O$_4$ and CdFe$_2$O$_4$ are normal cubic spinels.[5,6] The ferric ions occur at the octahedral B sites (point symmetry $\bar{3}m$), whereas Zn^{2+} and Cd^{2+} are located at the tetrahedral A sites (point symmetry $\bar{4}3m$). Oxides of the spinel type may be considered to be predominantly ionic.[7–9] Hudson and Whitfield used the point-dipole model to calculate the quadrupole coupling constants from the relation

$$e^2QV_{ZZ}^{(n)} = e^2Q(1-\gamma_\infty)V_{ZZ}. \qquad (1)$$

Here, $e^2QV_{ZZ}^{(n)}$ is the quadrupole coupling constant, Q is the nuclear quadrupole moment, and $V_{ZZ}^{(n)}$ is the electric field gradient (positive second derivative of the potential) at the nucleus. γ_∞ is the Sternheimer antishielding factor of Fe^{3+} and V_{ZZ} is the external field gradient at the Fe^{3+} position in the crystal. Since the sign of the field gradient was not known and because of additional ambiguities in the calculations it was concluded that the field gradient is "almost certainly negative in CdFe$_2$O$_4$ but may well be positive in ZnFe$_2$O$_4$." Yagnik and Mathur observed a monotonic increase of the quadrupole coupling constant in solid solutions from ZnFe$_2$O$_4$ to CdFe$_2$O$_4$.

They therefore concluded that the sign of the field gradient should be the same in both spinels. Were the field gradients in the two ferrites of opposite sign, the quadrupole coupling constant should assume a minimum value somewhere in the system. However, their assumption of a negative field gradient was speculative since they used an incorrect oxygen parameter for ZnFe$_2$O$_4$.

The aim of the present investigation was to take Mössbauer spectra of ZnFe$_2$O$_4$ and CdFe$_2$O$_4$ in an applied magnetic field in order to determine the sign of the quadrupole coupling constants experimentally and to analyze their magnitudes in the light of the observed isomer shifts and the point-multipole model. The lattice sums which are needed for the point-multipole model depend critically on the atomic coordinates in the crystal structure.[10,11] Therefore, more recent data on the crystal structures and a rapidly converging summation technique were used. The calculation of field gradients in normal spinels is straightforward since the cations occupy special positions, with all coordinates fixed by symmetry, and the anion positions have only one parameter. Because of the low Néel points of ZnFe$_2$O$_4$ and CdFe$_2$O$_4$[12,13] complications which arise from the magnetic hyperfine interactions[14] are not present in the spectra at 298°K. Moreover, the field gradient at the Fe^{3+} sites is axially symmetric. The magnitudes of the nuclear quadrupole coupling constants of ^{57}Fe can therefore be determined with precision. On the basis of the presumed high degree of ionicity these two structures appear to provide interesting cases for testing the ionic point-multipole model.

EXPERIMENTAL RESULTS

Polycrystalline samples were prepared by intimately mixing ZnCO$_3$ and Fe$_2$O$_3$, CdO, and Fe$_2$O$_3$, respectively, in stoichiometric amounts, pressing the powders into pellets, sintering at 800°C and regrinding. The powders

TABLE I. Chemical composition and ^{57}Fe hyperfine parameters of ZnFe₂O₄ and CdFe₂O₄ at 298°K.

Spinel	Lattice constant (Å)	Oxygen parameter u	Quadrupole splitting Δ [a] (mm/sec)	Isomer shift[b] (mm/sec)	Linewidth (FWHH) (mm/sec)	Area ratio[c]
ZnFe₂O₄ [d]	8.43	0.385	0.333 (0.001)[f]	0.350 (0.006)	0.258 (0.001)	1.056 (0.002)
CdFe₂O₄ [e]	8.71	0.389	0.784 (0.001)	0.368 (0.006)	0.330 (0.002)	1.056 (0.002)

[a] $\Delta = \frac{1}{2}e^2qQ$ $(\eta=0)$.
[b] Relative to metallic iron absorber.
[c] High velocity peak vs low velocity peak.

[d] Zn₁.₀₀₄Fe₁.₉₉₂O₄.
[e] Cd₁.₀₀₆Fe₁.₉₉₀O₄.
[f] Numbers within parentheses are standard deviations (neglecting systematic errors).

were then repressed into pellets and fired at 1200°C, quenched in air, and ground into a fine powder; this process was repeated until a pure phase was obtained.

The final phases were analyzed using x-ray diffraction and wet chemical analyses. The oxygen parameter u of CdFe₂O₄ was determined from a large number of x-ray diffraction traces using iron radiation and a proportional counter. The peak areas were measured by planimetry. Lorentz polarization, anomalous dispersion, etc., were corrected according to standard techniques. u was found to be 0.389±0.005.

The chemical composition of the samples was determined by (1) dissolving the samples in HCl, (2) separating Cd(Zn) from Fe, and (3) titrating Cd(Zn) with EDTA, and Fe with Ce⁴⁺. The deviations from stoichiometric composition are very small (Table I).

The Mössbauer resonant absorption spectra were obtained with the constant acceleration technique using a 400-channel analyzer as described previously.[15,16] The spectra were fitted by a least-squares technique.[17,18] The peak heights, widths, and positions of a presumed two-line spectrum of Lorentzians, and the off-resonant count rate were independently varied until $1 \leq \chi^2 \leq 1.5$ per data point (seven adjustable parameters). The ^{57}Fe quadrupole coupling constants and isomer shifts are in agreement with those previously reported.[1–4] The area ratios are very close to 1, and the linewidths are small; very little, if any, iron therefore occupies foreign sites. The spectra of ZnFe₂O₄ and CdFe₂O₄
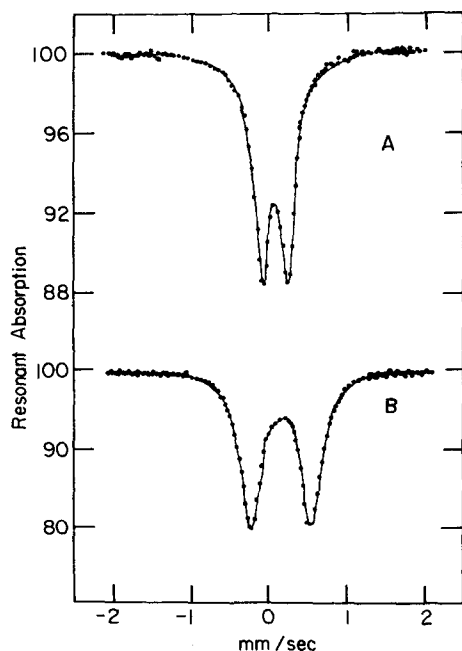

FIG. 1. Mössbauer absorption spectrum of ^{57}Fe in ZnFe₂O₄ (A) and CdFe₂O₄ (B) at 298°K. The solid lines are least-squares fits of Lorentzians assuming seven variables.
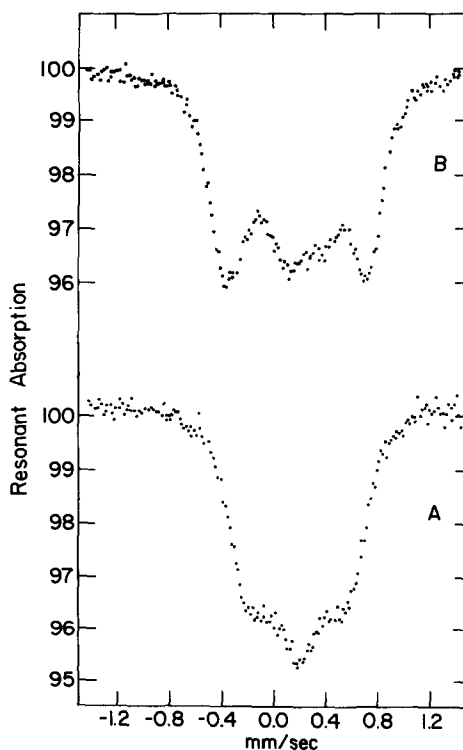

FIG. 2. Mössbauer absorption spectra of ZnFe₂O₄ in applied magnetic fields of 24 kG (A) and 37 kG (B). The rather weak line at +0.4 mm/sec is to be noted.
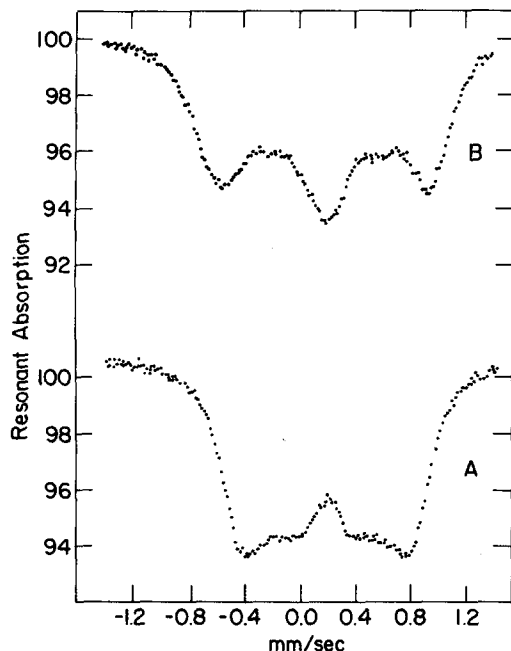
FIG. 3. Mössbauer absorption spectra of $CdFe_2O_4$ in applied magnetic fields at 24 kG (A) and 37 kG (B). The asymmetry of the central line and the relative widths of the two outer lines are to be noticed. The line in the negative velocity region is broader in both spectra.

at 298°K, in the absence of an applied magnetic field, are shown in Fig. 1. The ^{57}Fe parameters determined from the final fits are presented in Table I.

Spectra were also recorded at 298°K in external magnetic fields of 24 and 37 kOe applied parallel to the direction of propagation of the gamma ray (Figs. 2 and 3). These spectra were computed using the experimental quadrupole coupling constants and applied fields by a direct diagonalization of the Hamiltonian. For this the Gabriel–Ruby program[19] was used. The computed spectra for positive and negative signs of the quadrupole interaction are presented in Figs. 4 and 5. Inspection of these figures shows that the quadrupole coupling constant is *negative* for both $CdFe_2O_4$ and $ZnFe_2O_4$. It also follows from the relation (1) that V_{ZZ} must be negative in both spinels.

IONIC FIELD GRADIENTS IN SPINEL STRUCTURES

The electrostatic potentials and their first and second derivatives at the atomic positions in crystal structures of the spinel type are determined completely by six independent potential components V_i. Here, the terminology of Ref. 20 is used. V_1 and V_2 are the potentials at the cation positions A and B, respectively, and V_3 is the potential at the anion position. V_4 is the derivative $\partial V/\partial x$ at the B sites, etc., where x, y, z are chosen parallel to the cubic crystal axes. The six potential components are presented in Table II. The gradient of the potential at

the anion sites (point symmetry $\bar{3}m$) is parallel to a threefold axis in the direction $\mathbf{r}$, and its magnitude, V_r, is $V_r=\sqrt{3}V_5$. The maximum eigenvalue of the second derivative, V_{ZZ}, at the B sites is $V_{ZZ}=V_{rr}=2V_4$. The maximum eigenvalue of the second derivative at the anion sites is equal to $2V_6$.

If the ideal ionic model is assumed, the potential components V_i are interrelated to each other by the equation

$$V_i = V_i{}^M + \sum_{j=4}^{6} K_{ij}\alpha_j V_j, \qquad (2)$$

where $\alpha_4 = -\alpha_Q$ of the cation at the B sites, $\alpha_5 = -\alpha_D$ and $\alpha_6 = -\alpha_Q$ of the anion. α_D and α_Q are the dipole and quadrupole polarizabilities, respectively, of the ion in question. $V_i{}^M$ and K_{ij} are purely crystallographic parameters which are determined by the geometry of the crystal structure and depend only on the lattice constant and the parameter u of the anion position. The K_{ij} factors represent the contributions to the potential component at the site in question of a lattice composed of unit dipoles or unit quadrupoles. $V_i{}^M$ and K_{ij} are obtained from lattice summations carried out by expanding the Ewald sums for the Madelung potential in spherical harmonics.[20] Calculations were made for various values of u in order to illustrate the sensitivity of the monopole terms $V_i{}^M$ and K_{ij} factors on the crystal structure. The monopole terms $V_i{}^M$ and the factors K_{ij} for $ZnFe_2O_4$ and $CdFe_2O_4$ are presented in Tables III and IV.

DISCUSSION

One of the serious problems in applying the ionic model is the critical dependence of the point charge contribution to the field gradient, $V_{ZZ}{}^M$, on the oxygen
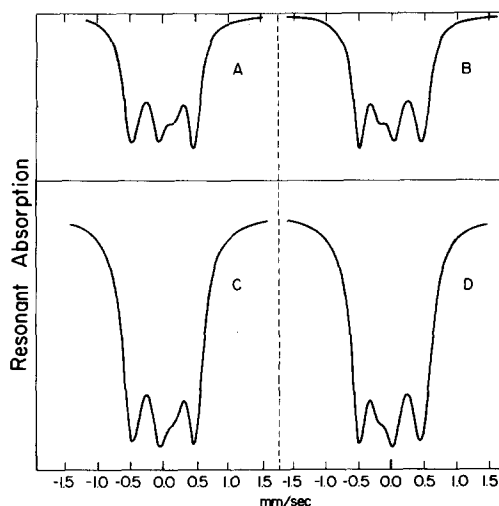

FIG. 4. Theoretical spectra for $ZnFe_2O_4$. A quadrupole splitting $\Delta=0.35$ mm/sec (negative in A, C; positive in B, D), an external field of 37 kG, and two different linewidths (0.25 mm/sec in A, B; 0.30 mm/sec in C, D) were assumed. A and C correspond to Fig. 2, B.

parameter u. This parameter is known for $ZnFe_2O_4$ from neutron diffraction experiments[21,22]: $u=0.3855\pm$ 0.0005. The calculated monopole contribution $V_{ZZ}{}^M$ to V_{ZZ} is $+0.497\pm10^{14}$ esu. Hudson and Whitfield reported $+0.5\times10^{14}$ esu ($u=0.385$). Our experimental value for V_{ZZ} obtained from Eq. (1) is -0.527×10^{14} esu, using $\gamma_\infty=-9.14$ [23] and $Q=0.20$ b. For $CdFe_2O_4$, u is less accurately determined from x-ray diffraction experiments: $u=0.386$,[24] and $u=0.389\pm0.005$ (this work). The calculated monopole values are $V_{ZZ}{}^M=+0.331\times10^{14}$ esu, and -0.172×10^{14} esu, respectively (Table III). Our experimental V_{ZZ}, using the same values for γ_∞ and Q as in $ZnFe_2O_4$, is -1.24×10^{14} esu. Hudson and Whitfield calculated $V_{ZZ}{}^M$ in $CdFe_2O_4$ for $u=0.393$ and found a strongly negative value for $V_{ZZ}{}^M$ which led to an apparent agreement with the experimental field gradient. But $u=0.393$ is definitely too large, and $V_{ZZ}{}^M$ is undoubtedly almost vanishing in $CdFe_2O_4$. Thus, it is clear that the simple monopole, point-ion model cannot account for either signs or magnitudes of the field gradients in $ZnFe_2O_4$ and $CdFe_2O_4$.

If the contributions from the electric dipole and quadrupole moments of the oxygen ions are included, the agreement between calculated and experimental V_{ZZ} is greatly improved. For this the system of simultaneous equations (2) must be solved using the K factors of Table IV and the electronic polarizabilities. The predominant contribution to the field gradient is due to the oxygen dipole moments because of the large factor K_{45}. All other K factors are significantly smaller. The dipole moments of the cations and the quadrupole moments of Zn^{2+} and Cd^{2+} are zero because of crystal symmetry. The contribution of the oxygen quadrupole moments is small since K_{64}, K_{65}, and K_{66} are approximately 10 times smaller than K_{45}. The effect of quadrupole moments will therefore not be considered in the final calculations. Thus the only polarizability needed is the dipole polarizability α_D of the oxygen ion. Unfortunately it is not well known. Taylor and Das used $\alpha_D=2.19$ Å³ in their study of BeO.[11] Brun and Hafner[10] calculated α_D for spinel

FIG. 5. Theoretical spectra of $CdFe_2O_4$. A quadrupole splitting $\Delta=0.80$ mm/sec (positive in A, negative in B), an external field of 37 kG, and a linewidth of 0.35 mm/sec were assumed. (B) corresponds to Fig. 3, B.

TABLE II. Electrostatic potential components of spinel.[a]

		$i=$			$ij=$				
		x	y	z^{b}	xx	xy	xz	yy	yz
$V(A)$	V_1								
$V(B)$	V_2								
$V_{ij}(B)$					0	V_4	V_4	0	V_4
$V(O^{2-})$	V_3								
$V_i(O^{2-})$		V_5	V_5	V_5					
$V_{ij}(O^{2-})$					0	V_6	V_6	0	V_6

[a] Terminology of Ref. 20.

[b] x, y, z are parallel to the cubic crystal axes.

$MgAl_2O_4$ from the refractive index and obtained $\alpha_D=1.51$ Å³. Studies of the electric field gradient in oxides generally yield values between 0.8 and 1.5 Å³. In our case the field gradients in $ZnFe_2O_4$ and $CdFe_2O_4$ were calculated using $\alpha_D=0.8$ Å³, $\alpha_D=1.51$ Å³, and $\alpha_D=2.19$ Å³, since the effective polarizability is almost certain to be within this range. The results are shown in Table V. Best agreement is obtained with the rather low value $\alpha_D=0.8$ Å³ and the parameter $u=0.389$ for $CdFe_2O_4$. This α_D may be compared with $\alpha_D=0.9$ Å³ reported for SnO^{25}; but in most ionic oxides α_D was found to be larger.[25] At any rate, the oxygen dipole moments definitely determine the negative signs of the field gradients in $ZnFe_2O_4$ and $CdFe_2O_4$, as observed previously in $MgAl_2O_4$.[10] This is due primarily to the generally large, positive value of factor K_{45} (Table IV) which is, as the other K factors, not sensitive to the oxygen parameter in spinels. However, the apparently close agreement between experimental and calculated field gradients for $\alpha_D=0.8$ Å³ may not be significant. If a larger value for α_D is chosen, or if a positive quadrupole polarizability for O^{2-} is introduced, the discrepancy from the experimental field gradient will become greater for $ZnFe_2O_4$ than for $CdFe_2O_4$. Nevertheless it is concluded that the point-multipole model accounts for the sign and major part of magnitude of the field gradients, although precise calculations cannot be made as long as accurate values for Q, γ_∞, and the electronic polarizabilities are not available.

Inspection of the apparent isomer shifts in Table II leads one to the conclusion that the ionic model should not be equally satisfactory in accounting for the field gradients in $CdFe_2O_4$ and $ZnFe_2O_4$. There are three contributions to the observed total shift (center of gravity of the ⁵⁷Fe doublet): (i) isomer shift, (ii) second-order Doppler effect (SOD), and (iii) zero point motion shift (ZPM). The total shift of ⁵⁷Fe in $CdFe_2O_4$ is greater by 0.018 ± 0.008 mm/sec than that in $ZnFe_2O_4$ (Table II). If the SOD and ZPM shifts at 298°K are the same for these two materials, then this difference in isomer shifts would be due to a greater s-electron density of the ⁵⁷Fe nucleus in $ZnFe_2O_4$
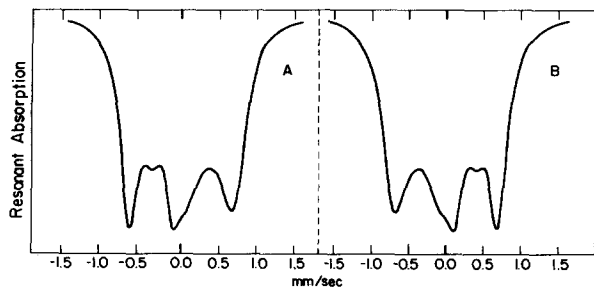
TABLE III. Nominal point charge potential components (first and second derivatives) in $ZnFe_2O_4$ and $CdFe_2O_4$.[a]

Potential component	$ZnFe_2O_4$ $a_0 = 8.44$ Å		$CdFe_2O_4$ $a_0 = 8.69$ Å				Units
	u 0.385	u 0.387	u 0.388	u 0.389	u 0.390	u 0.393	
$V_4^M = \frac{1}{2} V_{zz}^M (Fe^{3+})$	0.2486	0.0828	-0.0030	-0.0839	-0.1668	-0.4280	10^{14} esu
$V_5^M = (1/\sqrt{3}) V_z^M (O^{2-})$	0.8889	0.8429	0.7711	0.7455	0.7184	0.6592	10^6 esu
$V_6^M = \frac{1}{2} V_{zz}^M (O^{2-})$	0.6414	0.4860	0.3724	0.2884	0.2232	-0.0101	10^{14} esu

[a] If expressed in units of the lattice constant a_0, these values are generally correct for any normal 2^+, 3^+ spinel. The conversion formula is $V_i^M (e \times a_0^{-n}) = a_0^n V_i^M (e \times cm^{-n})$; $i = 4, 5, 6$.

than in $CdFe_2O_4$. From the variation of the observed shifts with the Fe–O internuclear separations in other spinels, it is concluded that the Fe–O bond in $ZnFe_2O_4$ is more covalent than the Fe–O bond in $CdFe_2O_4$. The Fe–O internuclear separation is 2.064 Å in $CdFe_2O_4$ and 2.018 Å in $ZnFe_2O_4$.

We can be reasonably confident, though, that the contributions from the SOD and ZPM shifts in $CdFe_2O_4$ and $ZnFe_2O_4$, are sufficiently alike and that differences in the 298°K isomer shifts reflect primarily differences in charge density. Moreover, it appears that the difference in the isomer shifts may reflect something less than the full difference in the s-electron densities at the nucleus. Kündig[26] has determined the temperature coefficients of the isomer shifts in Co_3O_4 to be $-(6.18\pm0.14) \times 10^{-4}$ mm/sec·°K for B-site Fe^{3+} and $-(6.15\pm0.28) \times 10^{-4}$ mm/sec·°K for A-site Fe^{3+} between 80 and 600°K. Evans and Hafner[16] determined the temperature coefficient of the isomer shift of the ferric ions in $CuFe_2O_4$ between 300 and 500°K to be -6.2×10^{-4} mm/sec·°K at the B sites and -5.5×10^{-4} mm/sec·°K at the A sites. The difference between the contributions from the SOD shifts for B-site

ferric ions in $CdFe_2O_4$ and $ZnFe_2O_4$ is expected to be considerably less than the difference between the SOD shifts of an A-site ferric ion and a B-site ferric ion in spinels, which is approximately 0.02 mm/sec at 298°K. This expectation is confirmed by the fact that the temperature coefficients are identical for the B-site ferric ions in Co_3O_4 and $CuFe_2O_4$ within the experimental error. In addition, the shorter Fe–O distance in $ZnFe_2O_4$ compared to $CdFe_2O_4$ is indicative of a smaller mean-square vibrational displacement, $\langle x^2 \rangle$, at all temperatures. This would lead to a smaller value for the magnitude of the temperature coefficient of the isomer shift for $ZnFe_2O_4$ than for $CdFe_2O_4$. Thus the difference in the s-electron densities at the nucleus (and the difference in the charge status) of the ferric ions in $CdFe_2O_4$ and $ZnFe_2O_4$ would be principally greater than that deduced from the observed shifts at 298°K. On the basis of the isomer shift considerations alone, we would not expect the ionic model to be equally adequate in explaining the field gradients in both of these materials.

Previous studies have indicated that the variations in the total s-electron density at the ^{57}Fe nucleus in

TABLE IV. Crystallographic K factors for $ZnFe_2O_4$ and $CdFe_2O_4$.[a]

K factor	$ZnFe_4O_4$ $a_0 = 8.44$ Å		$CdFe_2O_4$ $a_0 = 8.69$ Å			Units
	u 0.385	u 0.387	u 0.388	u 0.390	u 0.393	
K_{44}	-0.0303	-0.0303	-0.0261	-0.0261	-0.0261	10^{40} cm^{-5}
K_{45}	0.9958	1.0487	0.9569	1.0058	1.0802	10^{32} cm^{-4}
K_{46}	0.5159	0.5287	0.4620	0.4711	0.4816	10^{40} cm^{-5}
K_{54}	-0.1128	-0.1183	-0.1077	-0.1125	-0.1193	10^{32} cm^{-4}
K_{55}	0.4168	0.4230	0.3942	0.4016	0.4150	10^{24} cm^{-3}
K_{56}	0.0277	0.0335	0.0323	0.0381	0.0473	10^{32} cm^{-4}
K_{64}	-0.1634	-0.1614	-0.1383	-0.1351	-0.1284	10^{40} cm^{-5}
K_{65}	0.0821	0.1001	0.0973	0.1145	0.1423	10^{32} cm^{-4}
K_{66}	0.1309	0.1357	0.1199	0.1255	0.1359	10^{40} cm^{-5}

[a] If expressed in units of the lattice constant a_0, these factors are generally correct for any normal or inverse spinel. They are independent of the net charges. The conversion formula is $K_{ij}(a_0^{-n}) = a_0^n K_{ij}(cm^{-n})$.

TABLE V. Measured[a] and calculated electric field gradients in $ZnFe_2O_4$ and $CdFe_2O_4$ (nominal charges).

Spinel	Oxygen parameter u	$\alpha_D(O^{2-})$ (Å^3)	$V_{ZZ}=2V_4$ at Fe^{3+} position			
			Monopole (10^{14} esu)	Dipole (10^{14} esu)	Total (10^{14} esu)	Exptl (10^{14} esu)
$ZnFe_2O_4$	0.385	0.80	0.4972	−1.062	−0.565	−0.527
		1.51	0.4972	−1.640	−1.143	
		2.19	0.4972	−2.027	−1.530	
$CdFe_2O_4$	0.388	0.80	−0.0060	−0.897	−0.903	
		1.51	−0.0060	−1.397	−1.403	
		2.19	−0.0060	−1.734	−1.740	
	0.389	0.80	−0.1678	−0.888	−1.056	−1.24
		1.51	−0.1678	−1.380	−1.548	
		2.19	−0.1678	−1.712	−1.880	

[a] $\gamma_\infty(Fe^{3+}) = -9.14$, $Q(^{57}Fe) =0.20$ barn.

TABLE VI. Point charge potential components (first and second derivatives) in $ZnFe_2O_4$ and $CdFe_2O_4$ assuming reduced charges.

Charge state	Spinel[a]	Oxygen parameter u	$V_4^M=\frac{1}{2}V_{ZZ}^M$ (Fe^{3+}) (10^{14} esu)	$V_5^M=(1/\sqrt{3})V_Z^M$ (O^{2-}) (10^6 esu)	$V_6^M=\frac{1}{2}V_{ZZ}^M$ (O^{2-}) (10^{14} esu)
Nominal	$ZnFe_2O_4$	0.385	0.2486	0.8889	0.6414
	$CdFe_2O_4$	0.389	−0.0839	0.7455	0.2884
$Zn^{2.00+}Fe^{2.90+}O^{1.95-}$	$ZnFe_2O_4$	0.385	0.2199	0.8136	0.6542
	$CdFe_2O_4$	0.389	−0.1022	0.6787	0.3165
$Zn^{1.80+}Fe^{3.00+}O^{1.95-}$	$ZnFe_2O_4$	0.385	0.3092	1.0234	0.5376
	$CdFe_2O_4$	0.389	−0.0204	0.8693	0.2134

[a] $ZnFe_2O_4$: $a_0=8.44$ Å; $CdFe_2O_4$: $a_0=8.69$ Å.

TABLE VII. Measured and calculated electric field gradients in $ZnFe_2O_4$ and $CdFe_2O_4$ (reduced charges).

Charge state	Oxygen parameter u	$\alpha_D(O^{2-})$ (Å^3)	$V_{ZZ}=2V_4$ at Fe^{3+} position			
			Monopole (10^{14} esu)	Dipole (10^{14} esu)	Total (10^{14} esu)	Exptl
$Zn^{2.00+}Fe_2^{2.90+}O_4^{1.95-}$	0.385	0.80	0.4398	−0.9722	−0.5324	−0.527
	0.385	1.51	0.4398	−1.5016	−1.0618	
	0.385	2.19	0.4398	−1.8550	−1.4152	
$Cd^{2.00+}Fe_2^{2.90+}O^{1.95-}$	0.389	0.80	−0.2044	−0.8082	−1.0126	−1.24
	0.389	1.51	−0.2044	−1.2566	−1.4610	
	0.389	2.19	−0.2044	−1.5588	−1.7632	
$Zn^{1.80+}Fe^{3.00}O^{1.95-}$	0.385	0.80	0.6184	−1.2228	−0.6044	
	0.385	1.51	0.6184	−1.8890	−1.2706	
	0.385	2.19	0.6184	−2.3334	−1.715	
$Cd^{1.80+}Fe^{3.00}O^{1.95-}$	0.389	0.80	−0.0408	−1.0354	−1.0762	
	0.389	1.51	−0.0408	−1.6092	−1.6500	
	0.389	2.19	−0.0408	−1.9964	−2.0372	

ferric spinels are mainly due to direct changes in the $4s$ electron density, i.e., central field covalency.[27] Thus, there is no change in the contribution to the field gradient from the d electrons as one goes from $ZnFe_2O_4$ to $CdFe_2O_4$; there may be a change in the radial extent of the d orbitals relative to the free ion but such expansions occur without any change in relative symmetry. Similar conclusions have been reached for other compounds which are either isostructural or have little variation in the local symmetry of the lattice sites occupied by iron.[28] The different isomer shifts for ^{57}Fe in $CdFe_2O_4$ and $ZnFe_2O_4$ are therefore believed to be due only to differences in the net charge of effectively spherical ions.

In order to analyze the effect of charge transfer from the oxygen ions to the A and B site cations, the potential components $V_4{}^M$, $V_5{}^M$, and $V_6{}^M$ have been computed assuming various reductions of the net ionic charges. Some of the results are presented in Tables VI and VII. B-site ions make a positive contribution to V_4. Decreasing the net charge on the B-site ions will therefore have the effect of making the calculated field gradient more negative. But V_5 at the oxygen position will also be reduced, and this will make the oxygen dipole contribution to the field gradient at the B sites smaller. Decreasing the net charge on the A-site cations will make the field gradient more positive; but the oxygen dipoles will be increased. The over-all effect of charge transfer on the field gradient is *small*. A reduction of the nominal charge of the ferric ions by 10% reduces the field gradient only by a few percent.

While there is considerable covalence in the B-site Fe–O bonds,[27] it is not so great that an ionic model is wholly inappropriate for describing the electrostatic charge distribution in spinels. For example, the magnitudes of the magnetic hyperfine fields at the ferric ion in spinel ferrites can be explained on the basis of the isolated free ion, which is slightly modified (10%) by covalent effects. In summary, we consider the observed difference in the isomer shifts as consistent with the nuclear quadrupole coupling constants which are interpreted in terms of the point-multipole model. This model accounts for the sign, and semiquantitatively for the magnitude and trend of the coupling constants. Some charge transfer from oxygen to iron is definitely present and probably greater in $ZnFe_2O_4$ than in $CdFe_2O_4$. Its effect on the field gradient is not critical. A more precise estimate of the effective ionic charges in these spinels from the nuclear quadrupole data is not feasible at this point since the electronic polarizabilities are not well known.

For this, the u parameters should also be measured with higher precision in order to definitely determine the critical value $V_{ZZ}{}^M$. Whether or not the present result is of general applicability in spinels will have to await further experimental studies.

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